THE CATALYTIC ACTIVITY OF ORGANOMETALLIC COMPLEXES IN COPROCESSING

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Keywords: coprocessing, organometallic complexes, coal liquefaction

ABSTRACT

The catalytic activity of molybdenum, nickel, and vanadium, generated *in situ* from their organometallic complexes, as well as a presulfided powdered NiMo/Al$_2$O$_3$ was evaluated in coal-oil coprocessing. The coprocessing reactions were conducted both thermally and catalytically with Illinois No. 6 coal and Khafji or Maya residuum. The activities of molybdenum, nickel, and vanadium present as metal sulfides for converting coal and upgrading petroleum residuum were compared, and the possibility of indigenous nickel and vanadium catalysis in coprocessing was explored.

INTRODUCTION

The coprocessing of coal with petroleum residuum simultaneously upgrades coal, coal liquids and residuum into higher quality products[1-3]. When compared to coal liquefaction, coprocessing is attractive for several reasons[4]. Coprocessing uses a sufficient amount of low-cost petroleum residuum as the processing solvent without the extensive requirement of solvent recycling so that it produces larger volumes of hydrocarbon liquids than does the liquefaction of coal alone. Because coal is partially soluble in asphalt and residuum, less severe reaction conditions are required in coprocessing than in coal liquefaction. Therefore, coke formation is also reduced. In addition, coprocessing can utilize the existing upgrading facilities used for petroleum refining.

Catalytic coprocessing is more desirable than thermal coprocessing[5]. The role of the catalyst in coprocessing is substantial. The amount of coal conversion, the extent of heteroatom removal and saturation of aromatic compounds, and the product distribution in terms of the solubility of fractions, such as oil, asphaltenes, preasphaltenes and insoluble organic matter (IOM), in catalytic coprocessing is influenced by the catalyst used. This experiment evaluated and compared the effects of catalytically active species of Mo, Ni and V generated *in situ* from their organometallic complexes in a sulfur-rich environment on the upgrading of coal and petroleum residuum in coal-oil coprocessing.

Upgrading of coal and petroleum residuum may be achieved by several types of hydrogenation reactions: hydrogenolysis of carbon-carbon bonds or carbon-heteroatom bonds, producing smaller molecular structures, hydrogenation of compounds containing aromatic rings, producing more saturated hydrocyclic compounds, and removal of heteroatoms (S, N, O), producing more environmentally acceptable products with lower sulfur, nitrogen and oxygen contents. From past experience in hydrogenation reactions with model compounds[6,7], each

metal species is expected to show different catalytic activity and selectivity for various types of hydrogenation reactions occurring in coal-oil coprocessing. In this experiment, the catalytic activity and selectivity of different metals in upgrading actual coal and residuum in coprocessing reactions are compared. These experimental results are expected to be useful in evaluating the degree to which the catalytic character of each metal species is attributable to specific types of hydrogenation reactions in coprocessing. The possible catalytic activity of Ni and V indigenous to the residuum used as the solvent in coprocessing is also discussed.

EXPERIMENTAL

Feed Materials. Khafji and Maya petroleum residua and Illinois No.6 coal were selected as feed materials for coprocessing reactions. All of these materials were supplied by Amoco Oil Company. Khafji and Maya were used as received, but Illinois No. 6 coal was pulverized to 100 mesh and kept in a vacuum desiccator before use. The moisture content (6.3 wt%) and ash content (9.8 wt%) of Illinois No. 6 coal were obtained by Auburn University and used in the calculation of experimental results.

Catalyst. Organometallic complexes of transition metals, such as Mo, Ni and V, as well as a supported bimetallic NiMo/Al$_2$O$_3$, were used as coprocessing catalysts. The precursors of the active metal species of Mo, Ni and V were obtained in the form of an oil-phase naphthenate or octoate, or a solid-phase acetylacetonate and were supplied by Air Products, Shepherd Chemical, Strem Chemical, and Aldrich. The metal contents in the precursors supplied were 3 to 23 wt%. Each catalyst precursor was diluted by n-hexadecane to enhance its fluidity and to keep the metal content consistent in the precursor at 3 wt% of Mo or Ni and 1.5 wt% of V. A solid catalyst, Shell 324 NiMo/Al$_2$O$_3$, was presulfided in a heated gas stream of 10 vol% H$_2$S in H$_2$ and then pulverized to 150 mesh before use.

Thermal and Catalytic Reactions. The coprocessing reactions were performed in 56 cm^3 tubing bomb microreactors which were made of 316 stainless steel and horizontally oriented during reactions. Each coprocessing reaction was conducted with 3g of coal and 6g of Khafji or Maya residuum under reaction conditions of 1250 psig H$_2$ charged at ambient temperature (about 2820 psig at 400°C and 3000 psig at 425°C), 400°C or 425°C reaction temperature, one hour reaction time, and 550 cpm vertical shaking. In catalytic reactions, each catalyst paste or solid catalyst was introduced at the level of approximately 3000 ppm metal in the feed. In cases of organometallic complexes being used as catalyst precursors, elemental sulfur was added in an amount sufficient to produce metal sulfide *in situ* from each organometallic precursor; 0.038g for thermal reaction, 0.057g for Mo, 0.032g for Ni, and 0.077g for V.

Analysis. The coprocessing products from 3g coal and 6g residuum were fractionated by three different solvents: first, the oil fraction was extracted by hexane; next, the asphaltene fraction was extracted by toluene; finally, the preasphaltene fraction was extracted by tetrahydrofuran. About 9g of the whole product recovered from the coprocessing reaction was dissolved in a total of 450 ml hexane: the recovered product was dissolved in 150 ml hexane, sonicated for 4 minutes, centrifuged to separate hexane solubles and hexane from undissolved product materials, and then all of these procedures were repeated twice. Next, the hexane insolubles were dissolved in 450 ml toluene, and then the toluene insolubles separated from the extraction with toluene were dissolved in 450 ml tetrahydrofuran and extracted using similar procedures as with hexane. The amount of each fraction was compared in terms of gas, oil (hexane soluble), asphaltenes (hexane insoluble but toluene soluble), preasphaltenes

(toluene insoluble but tetrahydrofuran soluble), and insoluble organic matter (IOM - tetrahydrofuran insoluble) on a moisture, ash and catalyst free basis. The amount of gas product produced from the reaction was determined by H_2 analysis using a Varian 3700 gas chromatograph with a 15 m stainless steel column (1/8 inch OD) packed with mixed molecular sieve 13A (75 wt%) and molecular sieve 5A (25 wt%) and with a thermal conductivity detector. Reactions were usually duplicated, and the product distribution and the coal conversion were expressed as the average values. A statement of error is given in the tables.

RESULTS AND DISCUSSION

Efficacy of Coprocessing. The efficacy of coprocessing was evaluated by testing the effect of petroleum residuum on the extent of coal hydrogenation. Three grams of Illinois No. 6 coal were hydrogenated, both thermally and catalytically with Mo naphthenate, with 6g of different solvents: n-hexadecane, which appeared to be nearly nonreactive at the reaction conditions and was soluble in hexane, and Khafji and Maya residua, which were more reactive processing solvents. Each fraction produced from Illinois No. 6 coal was determined by subtracting the amount of that fraction produced from the hydrogenation reaction of 6g of Khafji or Maya alone at equivalent reaction conditions from the overall amount of the same fraction produced from the coprocessing reaction. Khafji and Maya produced more hexane and toluene solubles (oil and asphaltenes) than did n-hexadecane in both thermal and catalytic reactions. In the thermal reactions, the amount of oil and asphaltenes produced from Illinois No. 6 coal was about 7 wt% with n-hexadecane, 24 wt% with Khafji, and 13 wt% with Maya. In the catalytic reactions with Mo naphthenate, the amount of the same fractions produced from Illinois No. 6 coal was about 32 wt% with n-hexadecane, 56 wt% with Khafji, and 53 wt% with Maya. This result indicated that the petroleum residuum enhanced hydrogenation of heavy fractions produced from coal such as preasphaltenes to lighter fractions such as oil and asphaltenes or enhanced the dissolution of the fractions produced from coal in the extracting solvents.

Catalytic Activity of _In Situ_ Generated Metal Species in Coprocessing. The activities of Mo, Ni, and V catalysts generated _in situ_ from their organometallic complexes in coprocessing were evaluated and compared to each other and that of a presulfided powdered $NiMo/Al_2O_3$ catalyst at equivalent reaction conditions. The organometallic precursors of each metal were in the form of naphthenate, octoate, or acetylacetonate as shown in Table 1. The total active metal loading for each catalyst was about 3000 ppm of the feed materials. Even though sulfur was released from the feed materials during the reaction, a sufficient amount of elemental sulfur was added to generate metal sulfide from each precursor from the beginning of the reaction[8,9]. In the coal-Khafji coprocessing reactions, the Mo and Ni species were the most active for producing toluene solubles (oil and asphaltenes) and for converting coal. The different V species regardless of precursor structure used were the least active (Table 1).

As the reaction temperature was raised from 400°C to 425°C, the recovery of the products decreased from 97 - 100% at 400°C to 85 - 95% at 425°C. This decreased recovery most probably resulted from coking of the coal and residuum materials at the higher reaction temperature in both the thermal and catalytic reactions. In addition, gas production increased from 1 - 2.5 wt% at 400°C to 4 - 5.5 wt% at 425°C. Thermal reaction and catalytic reactions with Mo naphthenate and $NiMo/Al_2O_3$ converted more coal at higher temperature, but reactions with the other catalysts, especially vanadylacetylacetonate, showed reduced coal conversion at 425°C. In thermal and catalytic coprocessing reactions, the actual amount of oil

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and asphaltenes produced from coal at 425°C was nearly similar to or sometimes less than that at 400°C. Only Mo naphthenate appreciably enhanced the production of toluene solubles at higher temperature. These results indicated that a high reaction temperature frequently induced the production of more gaseous products and coke as well as other retrogressive reactions producing additional heavier fractions like preasphaltenes and IOM.

The high activity of Mo and Ni species and the low activity of V species were again confirmed in coal-Maya coprocessing reactions (Table 1). The hydrogen consumption in each reaction generally followed the activity of the catalyst used; more hydrogen consumption was observed with Mo, Ni, and NiMo/Al_2O_3 catalysts than with V catalysts or no catalyst.

Effect of Sulfur. Even though sulfur species, such as H_2S, were produced from feed materials during the reaction, elemental sulfur was usually added to the catalytic reactions to promote the production of metal sulfides in situ from the organometallic complexes. The effect of additional sulfur on the activity of the different catalysts, such as sulfur-sensitive Ni species[7] and sulfur insensitive Mo and V species, was evaluated in coal-Khafji coprocessing (Table 2). Elemental sulfur was added in an amount three times the quantity of sulfur required to produce a metal sulfide from each metal (MoS_2, Ni_3S_2 and V_2S_3). At both reaction temperatures, 400°C and 425°C, additional sulfur usually enhanced the production of oil and asphaltenes and the conversion of coal in both thermal and catalytic reactions except for the reactions with Ni octoate. The reason for the lowered activity of Ni octoate by sulfur has not yet been clearly explained. However, the activity of sulfur-sensitive Ni catalysts in coprocessing was not much affected by additional sulfur: the Ni species was still effective in converting coal and producing fractions of oil and asphaltenes.

Infrared Analysis of Coprocessing Products. Illinois No. 6 coal, residua, and various fractions extracted from coprocessing reactions have been analyzed qualitatively and quantitatively by conventional Fourier transform infrared (FTIR) spectrometry. The relationship between the catalytic activity observed and the infrared spectrum has been examined. The infrared spectrum of the oil fraction from the coprocessing reaction was very similar to that of the residuum used, predominantly showing aliphatic character with only a slight amount of aromatic character. However, the infrared spectrum of asphaltenes from the coprocessing reaction showed more coal character than oil, showing increased aromatic C-H stretch at 3050 cm^{-1}, aromatic ring stretch at 1585 cm^{-1}, and aromatic C-H out-of-plane bending at 860, 815, and 750 cm^{-1}. The infrared spectrum of preasphaltenes was the most similar to that of the coal used; the peaks indicating increased aromatic character and some other peaks indicating C-O stretch, C-C stretch, and O-H bending between 950 and 1300 cm^{-1}, that were not found in the spectrum of oil fraction, resembled the peaks in the spectrum of coal. The relationship between the activity of different catalysts and the infrared spectrum of the product obtained with each catalyst used is under study.

CONCLUSIONS

The activity of in situ generated molybdenum, nickel and vanadium catalysts as well as the effect of sulfur on them in upgrading coal and petroleum residuum was evaluated. Petroleum residua enhanced production of toluene solubles from coal compared to the nonreactive solvent, n-hexadecane. Catalytic coprocessing reactions usually produced more oil and asphaltenes than did thermal coprocessing.

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In the thermal coprocessing reactions, elemental sulfur introduced at a level of 0.004 g per gram of the mixed reactant of coal and residuum slightly enhanced the extent of oil production and produced less IOM fraction than the thermal reactions without additional sulfur. In the catalytic coprocessing reactions, *in situ* generated Mo and Ni species showed high levels of oil production and coal conversion. But *in situ* generated V species showed low activity similar to that of the additional sulfur in thermal reactions or even lower than the thermal reactions without sulfur depending on organic precursors of V used. A higher reaction temperature of 425°C did not activate V species as much as it did Mo and Ni species. The activities of *in situ* generated metal species (possibly metal sulfides) and a commercial presulfided NiMo/Al$_2$O$_3$ at the same metal loading of 3000 ppm for converting coal and simultaneously upgrading coal and residuum were observed in the following order.

Mo species ≈ Ni species > NiMo/Al$_2$O$_3$ > Thermal with sulfur ≥ V species.

Additional sulfur usually enhanced the activity of catalysts in coprocessing except for Ni species from Ni octoate. However, even in the presence of sulfur, the Ni species still showed high activity for coal conversion and oil and asphaltene production. These results indicated that indigenous nickel can be a possible coprocessing catalyst if its precursors in the feed materials are properly concentrated. V, which is usually more abundant in petroleum residuum than is Ni, appeared to have minor catalytic activity for converting coal and residuum to lighter fractions. However, the V sulfide species *in situ* generated showed high activity for heteroatom removal and partially saturating aromatic structures of model chemicals[10]. To understand this discrepancy between the activity of V sulfide species in model and actual coprocessing reactions, a study on the stoichiometry of active V sulfides *in situ* generated in both model and actual coprocessing reactions is required.

ACKNOWLEDGEMENTS

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Table 1. Coprocessing Reactions of Illinois No. 6 Coal and Khafji or Maya Residuum[1]

Reaction Conditions and Catalysts[2]	Product Distribution (wt%)[3]			Toluene Solubles[4]	Coal Conversion(%)
	Oil	Asp	Preasp		
Khafji					
No Reaction	57.5	13.3	2.0	70.8	NA[5]
400°C Reaction					
Thermal Reaction	56.1	17.5	11.4	73.6	56.3 ±2.0[6]
VO Acetylacetonate	55.1	17.9	11.3	73.0	53.2 ±3.4
NiMo/Alumina	58.3	17.4	10.2	75.7	61.9 ±0.6
Ni Acetylacetonate	59.1	18.9	16.6	78.0	86.9 ±2.5
Ni Octoate	61.6	18.4	11.6	80.0	78.0 ±0.4
Mo Naphthenate	61.8	22.3	9.6	84.1	86.4 ±6.7
425°C Reaction					
Thermal Reaction	50.8	17.0	13.4	67.8	60.0
VO Acetylacetonate	48.1	14.0	16.5	62.1	44.6
V Acetylactonate	53.5	17.5	13.6	71.0	69.2
V Naphthenate	55.2	16.9	13.0	72.1	65.0
NiMo/Alumina	60.5	16.0	7.5	76.5	68.5
Ni Octoate	60.2	16.8	9.8	77.0	72.4
Ni Acetylacetonate	60.5	18.7	11.4	79.2	84.8
Ni Naphthenate	62.5	17.3	6.4	79.8	72.4
Mo Octoate	66.7	17.0	3.6	83.7	77.0
Mo Naphthenate	70.3	20.4	3.3	90.5	95.0
Maya					
No Reaction	46.4	23.7	1.6	70.1	NA[5]
400°C Reaction					
Thermal Reaction	49.9	18.7	9.9	68.6	37.4 ±0.2[6]
V Naphthenate	45.6	21.5	13.4	67.1	50.7 ±1.4
Ni Naphthenate	51.1	23.1	17.8	74.2	82.8 ±4.1
NiMo/Alumina	52.2	24.3	11.0	76.5	67.7 ±3.5
Mo Naphthenate	56.7	23.7	7.0	80.4	66.9 ±0.1

[1] Overall product distribution based on the fractions produced from both coal and residuum was compared. The reactions performed at 400°C were duplicated and sometimes repeated more than twice, and the results were expressed as the average values. The standard deviation ($\pm \sigma_n$) of each fraction varied in the range of zero to 1.9 wt% (usually zero to 0.7 wt%) with Khafji residuum and in the range of 0.1 to 3.2 wt% (usually 0.1 to 0.9 wt%) with Maya residuum. The reactions performed at 425°C were conducted once.

[2] Abbreviations: V(vanadium), VO(vanadyl), Ni(nickel), and Mo(molybdenum). Additional sulfur: 0.037g for thermal reaction, 0.080g for V and VO, 0.031g for Ni, and 0.058g for Mo.

[3] The products were fractionated into gas, oil, asphaltenes(Asp), preasphaltenes(Preasp), and IOM.

[4] Toluene solubles (oil and asphaltenes)

[5] NA: Not available

[6] Standard deviation ($\pm \sigma_n$) of coal conversion (%)

Table 2. Effect of Sulfur on Coal-Khafji Coprocessing[1]

Coprocessing at 400°C \	Thermal	VOAcAc	NiAcAc	NiOct	MoNaph
Without Sulfur					
Oil (wt%)	52.8±1.6	54.4±1.1	58.3±0.1	60.0±0.1	60.0±0.2
Asphaltenes (wt%)	17.2±0.3	17.4±1.5	19.0±0.3	18.1±0.9	20.0±0.4
Coal Conversion (%)	46.9±1.6	42.7±2.8	85.3±1.7	78.7±2.5	76.3±1.3
With Sulfur[2]					
Oil (wt%)	56.1±0.7	55.1±1.0	59.1±0.7	61.6±0.3	61.8±1.2
Asphaltenes (wt%)	17.5±0.2	17.9±1.2	18.9±0.0	18.4±0.0	22.3±1.9
Coal Conversion (%)	56.3±2.0	53.2±3.4	86.9±2.5	78.0±0.4	86.4±6.7

Coprocessing at 425°C \	Thermal	VOAcAc	NiAcAc	NiOct	MoOct	MoNaph
Without Sulfur						
Oil (wt%)	52.5	51.9	55.5	65.6	68.3	69.9
Asphaltenes (wt%)	14.0	12.9	17.7	16.6	15.3	18.0
Coal Conversion (%)	50.3	40.5	80.4	77.1	76.4	92.2
With Sulfur[2]						
Oil (wt%)	55.6	50.8	62.6	62.0	71.2	73.2
Asphaltenes (wt%)	15.4	13.2	17.8	16.0	14.7	18.4
Coal Conversion (%)	60.0	44.6	84.8	72.4	77.0	95.0

[1] The product distribution was expressed as the average values and standard deviations ($X \pm \sigma_n$) based on the fractions of overall products from both coal and residuum in coprocessing. The reactions performed at 400°C were duplicated and sometimes repeated more than twice, and the reactions at 425°C were performed once.
Abbreviations: VOAcAc (vanadium actylacetonate), NiAcAc (nickel acetylacetonate), NiOct (nickel octoate), MoOct (molybdenum octoate), and MoNaph (molybdenum naphthenate).
[2] Additional sulfur amount: 0.038g for thermal reactions, 0.080g for V, 0.031g for Ni, and 0.058g for Mo species.